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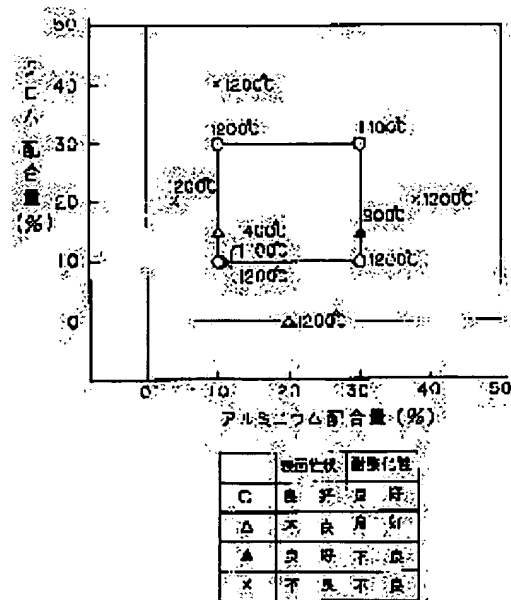
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(54) AL-CR COMPOSITE DIFFUSION COATING TREATING AGENT FOR TI ALLOY AND TREATMENT USING THE AGENT

(57)Abstract:

PURPOSE: To execute the Al-Cr composite diffusion coating treatment of a Ti alloy and to improve its oxidation resistance by constituting the above treating agent of specific wt.% of aluminum powder, chromium powder, ammonium chloride and the balance sintering-preventive powder.

CONSTITUTION: The Al-Cr composite diffusion coating treating agent for the Ti alloy is constituted, by weight %, of 10 to 30% aluminum powder, 10 to 30% chromium powder, 0.5 to 5% ammonium chloride and the balance the sintering-preventive powder. The Ti alloy is embedded into this treating agent and is heated at 1000 to 1300°C in a nonoxidative atmosphere, by which the Al-Cr diffusion coating layer is formed on the surface of the Ti alloy. Al-Cr alloy powder is compounded in place of a part or the whole of the aluminum powder or chromium powder. As a result, a precision polishing stage is simplified or saved.



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CLAIMS

[Claim(s)]

[Claim 1] The aluminum-Cr compound diffusion coating processing agent of Ti system alloy which consists of a 10 - 30wt% aluminium powder, a 10 - 30wt% chromium powder, a 0.5 - 5wt% ammonium chloride, and remainder sintering prevention powder.

[Claim 2] The aluminum-Cr compound diffusion coating approach of Ti system alloy characterized by forming an aluminum-Cr diffusion coating layer in the front face of the Ti system alloy concerned by laying Ti system alloy underground into the aluminum-Cr compound diffusion coating processing agent which consists of a 10 - 30wt% aluminium powder, a 10 - 30wt% chromium powder, a 0.5 - 5wt% ammonium chloride, and remainder sintering prevention powder, and heating at the temperature of 1000-1300 degrees C in a non-oxidizing atmosphere.

[Claim 3] The aluminum-Cr compound diffusion coating processing agent according to claim 1 which replaces with some or all of an aluminium powder or chromium powder, and blends aluminum-Cr alloy powder into the aluminum-Cr compound diffusion coating processing agent concerned, or the aluminum-Cr compound diffusion coating approach of Ti system alloy according to claim 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the art of heat-resistant Ti alloy which used the aluminum-Cr compound diffusion coating processing agent and its processing agent for forming an oxidation-resistant coat in the front face of Ti system alloy.

[0002]

[Description of the Prior Art] Ti alloy has small lightweight specific gravity, since a mechanical strength is high and corrosion resistance is good, it is widely used as a lightweight structural material and a corrosion resisting material, but in hot atmospheric air, the front face of Ti alloy oxidizes, and the oxide layer grows easily, and N and H are absorbed, and since it stiffens, service temperature is restricted to 500 degrees C or less. Then, in order to give the oxidation resistance of Ti alloy, aluminum enveloping layer is formed in front faces, such as unalloyed ti and Ti-6aluminum-4V alloy, the attempt using the oxidation depressor effect of aluminum enveloping layer is made, and the effectiveness that this aluminum enveloping layer mitigates hydrogen embrittlement is also accepted.

[0003] Moreover, there is a Ti-aluminum system alloy which contained aluminum 15 to 35% among the conventional heat-resistant Ti alloys, and usable oxidation resistance is shown in them in about 700-degree C atmospheric air. Although this alloy has an application suitable as a heat-resisting material in the stator vane stationary blade of a jet engine compressor, the blade for gas turbines for a generation of electrical energy, the turbine rotor for automobiles, etc., since heat-resistant temperature is low in addition, by laying underground and heating this alloy ingredient to the powder containing aluminium powder, aluminum enveloping layer is formed in that alloy front face, and the attempt which raises oxidation resistance by three layer of TiAl(s) is made (JP,1-111858,A).

[0004]

[Problem(s) to be Solved by the Invention] TiAl₃ formed by aluminum diffusion coating processing in elevated-temperature air 900 degrees C or more although oxidation resistance can be improved and service temperature could be made high by covering aluminum enveloping layer into Ti system alloy containing a high aluminum-Ti alloy The oxide film of a layer is TiAl₃, in order that adhesion may not be enough and may repeat exfoliation and playback. Since oxidation of a layer continues advancing, it is not enough as a heat-resisting material.

[0005] Conventionally, chiefly, although aluminum enveloping layer of Ti system alloy front face lays Ti system alloy ingredient underground into the processing agent which consists of aluminium powder, alumina powder, and an ammonium chloride and is formed in an elevated temperature by the diffusion coating approach which carries out long duration heating maintenance Usually by this approach, surface deterioration was produced on the surface of the enveloping layer, and it was uneconomical in order to need many chipping allowances of the surface polish for acquiring a smooth side in a precision heatproof member, therefore to make aluminum enveloping layer thick beyond the need. moreover, the components of a configuration with a complicated turbine rotor etc. -- receiving -- since precise surface polish processing is very difficult -- a front face -- the smooth enveloping layer needed to be formed.

[0006] Artificers improved the calorize processing by the conventional powder method for heat-resisting steel, and already proposed how aluminum diffusion coating processing agent which mixed chromium powder to the aluminium powder performs diffusion coating processing (Japanese Patent Application No. 3-99500). This approach forms a smooth and homogeneous calorize layer by mixing chromium powder to aluminium powder.

[0007] aluminum diffusion coating processing agent in which this invention contains the above-mentioned Cr powder -- other Ti-aluminum alloy and Ti system alloy -- applying -- oxidation resistance and a front face -- the knowledge which improves description tends to be acquired and it is going to offer the aluminum-Cr compound diffusion coating processing agent and its diffusion coating art for manufacture of the aluminum-Cr diffusion coating Ti system alloy excellent in oxidation resistance.

[0008]

[Means for Solving the Problem] The aluminum-Cr compound diffusion coating processing agent of Ti system alloy of this invention is characterized by consisting of 10 - 30wt% aluminium powder, a 10 - 30wt% chromium powder, a 0.5 - 5wt% ammonium chloride, and a remainder sintering inhibitor.

[0009] Moreover, the aluminum-Cr compound diffusion coating approach of Ti system alloy of this invention lays Ti system alloy underground into the aluminum-Cr compound diffusion coating processing agent which consists of 10 - 30wt% aluminium powder, a 10 - 30wt% chromium powder, a 0.5 - 5wt% ammonium chloride, and a remainder sintering inhibitor, and is characterized by heating at the temperature of 1000-1300 degrees C in a non-oxidizing atmosphere.

[0010] The aluminium powder and chromium powder in the above-mentioned aluminum-Cr compound diffusion coating processing agent may substitute an aluminum-Cr alloy for the part or all. In this case, the amount of aluminum and the amount of Cr(s) in the aluminum-Cr alloy concerned are added to aluminium powder and chromium powder, respectively, and it is adjusted so that it may go into the above-mentioned presentation-among processing agent range.

[0011]

[Function] When the aluminum-Cr compound diffusion coating processing agent containing aluminium powder and chromium powder performs diffusion coating processing on the front face of Ti alloy, at the temperature of 1000-1300 degrees C A part fuses aluminium powder and chromium powder, they serve as an aluminum-Cr alloy melt drop, the remainder lives together as an aluminum-Cr alloy solid-state, and an aluminum-Cr alloy melt drop and an aluminum-Cr alloy solid-state react with an ammonium chloride. $AlCl_3$ of a gas $CrCl_2$ It generates, and aluminum and Cr deposit on Ti alloy front face from these gases, spreading diffusion is carried out and an aluminum-Cr diffusion coating layer is formed. $TiAl_2$ which the amount of aluminum deposits to Ti alloy front face was reduced, and raised aluminum diffusion rate inside Ti alloy, and contained Cr by high temperature processing further in the aluminum-Cr diffusion coating layer by reducing aluminum activity by combination of Cr to the inside of the processing agent concerned The enveloping layer or $TiAl_3$ of phase single phase It is a phase to a surface layer $TiAl_2$ The enveloping layer of two phases which made the phase the inner layer is formed.

[0012] When not blending chromium into the processing agent concerned, only aluminum liquid phase of a low-melt point point generates, and it is the gaseous phase $AlCl_3$ with a high partial pressure. Since it moves to an alloy front face so much, it is $TiAl_3$ of a front face. A phase and $TiAl_2$ Although the crystal grain of a phase makes it big and rough and surface roughness becomes large By blending chromium powder, aluminum activity in aluminum-Cr melt and a solid-state falls, and it is $CrCl_2$. It is $AlCl_3$ by generation. A partial pressure is reduced and it is $TiAl_3$. Crystal grain, such as a phase, is made detailed and a front face is made smooth. $TiAl_3$ Cr contained in a phase may also be participating in detailed-ization.

[0013] Moreover, $TiAl_3$ in an aluminum-Cr diffusion coating layer Little ** rare ** Cr is $TiAl_3$ of the enveloping layer concerned to a phase. Since the oxidation rate of a layer is reduced remarkably, the oxidation resistance of Ti system alloy is improved. However, if it becomes high at about 8% or more of the Cr concentration in an enveloping layer concerned, oxidation resistance will get worse on the contrary. That is, spreading diffusion of the combination of the chromium powder in the processing agent concerned is carried out to the function to carry out homogenization smoothing of the aluminum-

Cr diffusion coating layer front face of Ti alloy, and to prevent surface roughness, and an aluminum-Cr diffusion coating layer, it raises Cr concentration, and has the function to improve oxidation resistance.

[0014] Although the amount of aluminium powder in the aluminum-Cr compound diffusion coating processing agent of this invention needs to secure 10 - 30%, at the less than 10% of the amounts of aluminium powder, dispersion produces an aluminum-Cr diffusion coating layer in surface section thickness thinly, and oxidation resistance is not acquired. Moreover, if it exceeds 30%, the surface dry area of an aluminum-Cr diffusion coating layer will arise, and a smooth side will not be acquired.

[0015] Moreover, although the chromium powder volume in the processing agent concerned needs 10 - 30%, at less than 10%, in an aluminum-Cr diffusion coating layer, an aluminum-Cr diffusion coating layer will be in a porous surface deterioration condition, and it will be contained [do not diffuse Cr,], and oxidation resistance falls. If chromium powder volume exceeds 30%, Cr concentration in an aluminum-Cr diffusion coating layer will rise, and surface deterioration will arise on a front face, and it will become porosity near the front face, and oxidation resistance will be got worse.

[0016] The sintering inhibitor in an aluminum-Cr compound diffusion coating processing agent works as support which distributes suitably and supports Ti alloy ingredient made distribute the melt drop and solid-state grain of an aluminum-Cr alloy homogeneity and laid underground. This sintering inhibitor has good alumina powder.

[0017] Moreover, it works as mentioned above as a migration object to Ti system alloy front face of aluminum and Cr, using an ammonium chloride as the fusing agent which carries out melting removal of the oxide affix of Ti alloy ingredient front face, and the loadings are made into 0.5 - 5%. If it blends exceeding 5%, since an ammonium chloride is sublimated and produces loss, it is not suitable.

[0018] If the temperature of aluminum-Cr compound diffusion coating processing is suitable and is lower than the processing temperature of 1000 degrees C, since aluminum and Cr will not fully be spread from Ti alloy front face but the aluminum-Cr compound diffusion coating layer formed will become thin, sufficient oxidation resistance is not acquired. [of the range of 1000 degrees C - 1300 degrees C] Moreover, if it exceeds 1300 degrees C, an aluminum-Cr alloy solid-state and the powder of a sintering inhibitor will adhere to Ti alloy front face, surface deterioration will be produced, and a smooth front face will not be obtained.

[0019]

[Example] The loadings of the aluminium powder of an aluminum-Cr compound diffusion coating processing agent and chromium powder were changed, aluminum-Cr compound diffusion coating processing was performed into the Ti-aluminum alloy, and the trial which forms an aluminum-Cr diffusion coating layer was performed.

[0020] Aluminium powder was adjusted 5 to 40%, and it adjusted chromium powder in 0 - 40% of range, and the aluminum-Cr compound diffusion coating processing agent considered the ammonium chloride as 0.5% of fixed combination, and prepared it as a sintering inhibitor of the remainder using alumina powder.

[0021] The Ti-34wt%aluminum alloy for heatproofs was used for Ti alloy, and, as for the test specimen, it was processed into the piece of a trial of a cylindrical configuration with a diameter [of 8mm], and a die length of 10mm.

[0022] The above-mentioned aluminum-Cr compound diffusion coating processing agent was inserted in the steel container, and the above-mentioned piece of a trial was laid underground into the processing agent concerned, and it heated in temperature of 900 degrees C - 1400 degrees C, it held in argon atmosphere gas for 10 hours, and aluminum-Cr compound diffusion coating processing was performed.

[0023] The shape of front planarity of the piece of a trial after this processing was observed, the thickness of an aluminum-Cr diffusion coating layer was measured by microscope observation of that cross section, and surface aluminum concentration and Cr concentration were further measured by EPMA.

[0024] The enveloping layer front face of the piece of a trial after aluminum-Cr compound diffusion coating processing had what presents a surface deterioration-like split face, and the thing which presents a beautiful smooth side. Then, the enveloping layer front face of the piece of a trial was observed with

the scanning electron microscope (SEM). Although drawing 2 (A) is the SEM photograph of the piece of a trial (sample number 1) which presented the split face, the granular object of about 100 micrometers of big and rough grain length projected and distributed over the front face is observed. Although the piece of a trial (sample number 2) of this drawing (B) has produced surface deterioration on the piece front face of a trial, a surface granular object is an example made detailed. This drawing (C) is the SEM photograph of the front planar good piece of a thing trial (sample number 10) which does not have surface deterioration, and has made the surface granular object minute with the particle size of 2 micrometers or less. It turned out that precise smoothing of the front face of the piece of a trial is carried out, so that the granular object on this front face of an enveloping layer made it detailed from the SEM observation result. That is, it depends for the shape of front planarity after aluminum-Cr compound diffusion coating processing on the particle size of a surface granular object.

[0025] Next, heating maintenance of the above-mentioned piece of a trial which carried out aluminum-Cr compound diffusion coating processing was carried out at the temperature of 1000 degrees C among atmospheric air for 100 hours, the anti-oxidation sex test was carried out, from the weight difference before and behind heating of the piece of a trial, oxidation increase in quantity was computed and the oxidation resistance of an aluminum-Cr diffusion coating layer was evaluated. The test result was collectively shown in Table 1.

[0026]

[Table 1]

試料 番号	処理剤量		処理温度	A l - C r 拡散被覆層				酸化増量 mg/cm ²
	Al粉	Cr粉		Al濃度	Cr濃度	層 厚	表 面	
1	20%	0%	1200 ℃	62.0%	0 %	180 μm	荒	4.8
2	10	40	1200	41.5	9.8	40	荒	25
3	5	20	1200	39.5	2	55	不均質	36
4	40	20	1200	63.2	0.8	140	荒	8.9
5	30	15	900	58.4	0	15	良	10.5
6	10	15	1400	57.0	1.8	160	荒	4.9
7	10	10	1100	57.8	0.5	60	良	3.0
8	10	10	1200	52.8	2.8	90	良	0.3
9	30	10	1200	60.0	0.8	140	良	1.0
10	10	30	1200	51.1	4.9	60	良	0.8
11	30	30	1100	62.2	8.9	100	良	3.3

* 1000℃×100時間大気中加熱

[0027] Moreover, it is drawing 1 which illustrated the shape of front planarity, and oxidation resistance in the relation between the amount of aluminium powder in an aluminum-Cr compound diffusion coating processing agent, and chromium powder volume. the inside of drawing -- oxidation increase-in-quantity 5 mg/cm² It had the following and it was judged that oxidation resistance was good.

[0028] The range surrounded as the continuous line in drawing 1 is the combination range of the aluminum-Cr compound diffusion coating processing agent of this invention. In the temperature of

1000-1300 degrees C, the shape of front planarity and oxidation-resistant both sides show that this combination range of a processing agent is good.

[0029] Next, it replaces with the whole quantity of aluminium powder and chromium powder, and the example which used the aluminum-Cr alloy powder is shown. 40%, 0.5% of ammonium chlorides and remainder alumina powder were blended, and the aluminum-Cr alloy powder (75% of aluminum contents, 25% of Cr contents) was made into the aluminum-Cr compound diffusion coating processing agent. This combination of an aluminum-Cr alloy powder is equivalent to combination of 30% of aluminium powder, and 10% of chromium powder.

[0030] The piece of a trial with a diameter [of 8mm] and a die length of 10mm of a Ti-34wt% aluminum alloy was laid under this processing agent, aluminum-Cr compound diffusion coating processing of 1200 degree-Cx 10 hours was performed to it, and the anti-oxidation sex test of 1000 degree-Cx 100 hours was performed to it after that. although a result is shown in Table 2 -- the front face of an aluminum-Cr compound diffusion coating layer -- description and oxidation resistance -- all are good.

[0031]

[Table 2]

試料 番号	AlCr合金粉		処理 温度	A l - C r 拡散被覆層				* 酸化増量 mg/cm ²
	Al量	Cr量		Al濃度	Cr濃度	層 厚	表 面	
2 1	30%	10%	1200℃	60.4%	1.0%	150 μ m	良	1.0

* 1 0 0 0℃×1 0 0時間大氣中加熱

[0032]

[Effect of the Invention] If aluminum-Cr compound diffusion coating processing of Ti system alloy is carried out by the aluminum-Cr compound diffusion coating processing agent which blended the chromium powder of this invention, oxidation resistance is improved by the aluminum-Cr diffusion coating layer containing Cr of Ti system alloy, and the maximum service temperature can be raised to 1050 degrees C in aluminum alloy Ti-14 to 36%.

[0033] Even if it does not carry out surface polish at all in using it, for example as a turbine blade since it can perform easily using an aluminum-Cr diffusion coating layer front face as the front face which cannot finish being smooth at coincidence Even when it can be used, without reducing the rotation effectiveness of a turbine and carries out surface precision polish A chipping allowance can be made thin, since it is not necessary to thicken an aluminum-Cr diffusion coating layer beyond the need, diffusion coating down stream processing can be simplified, and a precision polish process can be simplified or skipped.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing showing the relation of oxidation increase in quantity of the anti-oxidation sex test with the shape of the amount of aluminium powder in an aluminum-Cr compound diffusion coating processing agent, chromium powder volume, and front planarity after diffusion coating processing.

[Drawing 2] (A), (B), and (C) are a metal texture photograph (all scale-factor; 70) according respectively to the scanning electron microscope of the diffusion coating layer front face of the test piece after the aluminum-Cr compound diffusion coating processing processing about sample numbers 1, 2, and 10.

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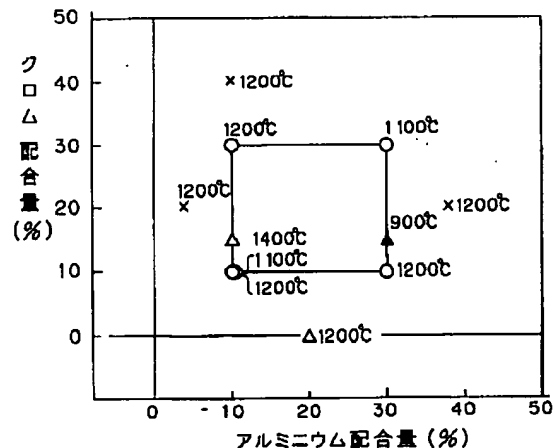
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(54)【発明の名称】 Ti系合金のAl-Cr複合拡散被覆処理剤及びその処理法

(57)【要約】

【目的】 一般に、Ti系合金は耐熱性に劣るが、表面にAl拡散被覆層を形成した合金が耐酸化性の向上に有効であり、特に耐熱性に優れたTi-14~36%Al合金にAl拡散被覆層を形成して、耐酸化性を改善する試みがなされている。しかし精密な耐熱部材として利用するには、さらに耐酸化性と被覆層の表面性状の改善が必要となっている。

【構成】 Al粉10~30%、Cr粉10~30%、塩化アンモニウム0.5~5%及びアルミナ粉残部からなるAl-Cr複合拡散被覆処理剤によって、1000~1300℃の温度でTi系合金の表面に拡散被覆処理を行う。処理剤中のCrの存在により、合金被覆層の表面が平滑化し、同時に耐酸化性を使用温度1050℃にまで向上する。



	表面性状	耐酸化性
○	良好	良好
△	不良	良好
▲	良好	不良
×	不良	不良

【特許請求の範囲】

【請求項1】 10～30wt%のアルミニウム粉末と10～30wt%のクロム粉末と0.5～5wt%の塩化アンモニウムと残部焼結防止粉末とから成るTi系合金のAl-Cr複合拡散被覆処理剤。

【請求項2】 10～30wt%のアルミニウム粉末と10～30wt%のクロム粉末と0.5～5wt%の塩化アンモニウムと残部焼結防止粉末とからなるAl-Cr複合拡散被覆処理剤中にTi系合金を埋設し、非酸化性雰囲気中で1000～1300℃の温度で加熱することにより、当該Ti系合金の表面にAl-Cr複合被覆層を形成することを特徴とするTi系合金のAl-Cr複合拡散被覆処理法。

【請求項3】 当該Al-Cr複合拡散被覆処理剤中に、アルミニウム粉末もしくはクロム粉末の一部もしくは全部に代えて、Al-Cr合金粉末を配合する請求項1記載のAl-Cr複合拡散被覆処理剤又は請求項2記載のTi系合金のAl-Cr複合拡散被覆処理法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、Ti系合金の表面に耐酸化性被膜を形成するためのAl-Cr複合拡散被覆処理剤とその処理剤を使用した耐熱性Ti合金の処理方法に関する。

【0002】

【従来の技術】Ti合金は、比重が小さく軽量で、機械的強度が高く耐食性が良好であるため、軽量の構造材料として、また耐食性材料として広く利用されているが、高温の大気中では、Ti合金の表面が酸化し、その酸化物層が容易に成長し、またNやHを吸収して、脆化するので、使用温度は500℃以下に限られる。そこで、Ti合金の耐酸化性を付与するため、純TiやTi-6Al-4V合金等の表面にAl被覆層を形成して、Al被覆層の酸化抑制効果を利用する試みがなされており、このAl被覆層が水素脆性を軽減する効果も認められている。

【0003】また、従来の耐熱性Ti合金には、15～35%Alを含有したTi-Al系合金があり、約700℃の大気中で使用可能な耐酸化性を示す。この合金は、ジェットエンジン圧縮機のステータベーン静翼や発電用ガスタービン用ブレード、自動車用のタービンロータなどに耐熱材料として好適な用途があるが、なお耐熱温度が低いので、アルミニウム粉を含む粉末にこの合金材料を埋設して加熱することにより、その合金表面にAl被覆層を形成して、TiAl₃層により耐酸化性を向上させる試みがなされている（特開平1-111858号）。

【0004】

【発明が解決しようとする課題】高Al-Ti合金を含むTi系合金にAl被覆層を被覆することによって耐酸

化性を改善し、使用温度を高くすることができるが、900℃以上の高温空気中では、Al拡散被覆処理で形成されたTiAl₃層の酸化皮膜は密着性が充分でなく、剥離と再生を繰り返すためにTiAl₃層の酸化は進行し続けるので、耐熱材料としては十分ではない。

【0005】Ti系合金表面のAl被覆層は、従来専ら、アルミニウム粉、アルミナ粉及び塩化アンモニウムからなる処理剤中にTi系合金材料を埋設して、高温に長時間加熱保持する拡散被覆処理法により形成されるが、この方法では、被覆層の表面に肌荒れを生じるのが普通で、精密耐熱部材では、平滑面を得るための表面研磨の削り代を多く必要とし、従って、Al被覆層を必要以上に厚くするため不経済であった。また、タービンロータ等の複雑な形状の部品に対しては、精密な表面研磨加工が非常に困難であるため、表面平滑な被覆層の形成が必要であった。

【0006】発明者らは、既に、耐熱鋼を対象にして、従来の粉末法によるカロライズ処理を改良して、アルミニウム粉末にクロム粉末を混合したAl拡散被覆処理剤により拡散被覆処理を行う方法を提案した（特願平3-99500）。この方法は、アルミニウム粉にクロム粉末を混合することにより、平滑で均質なカロライズ層を形成するものである。

【0007】本発明は、上記のCr粉末を含むAl拡散被覆処理剤を、Ti-Al合金その他Ti系合金に適用して耐酸化性と表面性状を改善する知見を得て、耐酸化性にすぐれたAl-Cr複合被覆Ti系合金の製造のためのAl-Cr複合拡散被覆処理剤及びその拡散被覆処理方法を提供しようとするものである。

【0008】

【課題を解決するための手段】本発明のTi系合金のAl-Cr複合拡散被覆処理剤は、10～30wt%のアルミニウム粉と10～30wt%のクロム粉末と0.5～5wt%の塩化アンモニウムと残部焼結防止剤とから成ることを特徴としている。

【0009】また、本発明のTi系合金のAl-Cr複合拡散被覆処理法は、10～30wt%のアルミニウム粉と10～30wt%のクロム粉末と0.5～5wt%の塩化アンモニウムと残部焼結防止剤とから成るAl-Cr複合拡散被覆処理剤中にTi系合金を埋設し、非酸化性雰囲気中で1000～1300℃の温度で加熱することを特徴とするものである。

【0010】上記Al-Cr複合拡散被覆処理剤中のアルミニウム粉とクロム粉は、その一部又は全部をAl-Cr合金に代替してもよい。この場合は当該Al-Cr合金中のAl量及びCr量を、それぞれアルミニウム粉及びクロム粉に加算して、上記処理剤中組成範囲に入るように調整される。

【0011】

【作用】アルミニウム粉とクロム粉とを含むAl-Cr

複合拡散被覆処理剤によりTi合金の表面に拡散被覆処理を行うと、1000~1300℃の温度では、アルミニウム粉とクロム粉は、一部は溶融してAl-Cr合金融液滴となり、残部はAl-Cr合金固体として共存し、Al-Cr合金融液滴とAl-Cr合金固体とが塩化アンモニウムと反応して、気体の $AlCl_3$ と $CrCl_2$ を生成し、これら気体からAl及びCrがTi合金表面に析出し拡散移動して、Al-Cr拡散被覆層を形成する。Al-Cr拡散被覆層中では、当該処理剤中へのCrの配合により、Al活量を低下させることにより、Ti合金表面へのAl析出量を低下させ、更に高温処理により、Ti合金内部へのAl拡散速度を高めて、Crを含有したTiAl₂相単相の被覆層又はTiAl₃相を表面層にTiAl₂相を内層とした2相の被覆層を形成する。

【0012】当該処理剤中にクロムを配合しない場合は、低融点のAl液相のみが生成し、分圧の高い気相 $AlCl_3$ が多量に合金表面に移動するので、表面のTiAl₃相とTiAl₂相の結晶粒が粗大化して、表面粗さが大きくなるが、クロム粉を配合することにより、Al-Cr融液及び固体中のAl活量が低下し且つ $CrCl_2$ の生成により $AlCl_3$ の分圧を低下させ、TiAl₃相などの結晶粒を微細化し、表面を平滑にする。TiAl₃相に含まれるCrも微細化に関与しているのかも知れない。

【0013】また、Al-Cr拡散被覆層中のTiAl₃相に少量含まれるCrは、当該被覆層のTiAl₃層の酸化速度を著しく低下させるので、Ti系合金の耐酸化性を改善する。但し、当該被覆層中Cr濃度約8%以上に高くなると返って耐酸化性は悪化する。即ち、当該処理剤中のクロム粉末の配合は、Ti合金のAl-Cr拡散被覆層表面を均質化平滑化して表面荒を防止する機能とAl-Cr拡散被覆層に拡散移動して、Cr濃度を高め、耐酸化性を改善する機能とを有するのである。

【0014】本発明のAl-Cr複合拡散被覆処理剤中のアルミニウム粉量は10~30%を確保する必要があるが、アルミニウム粉量10%未満ではAl-Cr拡散被覆層は、薄くかつ表面部厚みにばらつきが生じて、耐酸化性が得られない。また30%を超えると、Al-Cr拡散被覆層の表面荒れが生じ、平滑面が得られない。

【0015】また当該処理剤中のクロム粉量は10~30%を必要とするが、10%未満では、Al-Cr拡散被覆層が多孔性の肌荒れ状態となり、またAl-Cr拡散被覆層中にCrが拡散せず含まれないこととなり、耐酸化性が低下する。クロム粉量が30%を超えると、Al-Cr拡散被覆層中のCr濃度が上昇して表面に肌荒れが生じ、且つ表面近傍が多孔性となって、耐酸化性を悪化する。

【0016】Al-Cr複合拡散被覆処理剤中の焼結防止剤は、Al-Cr合金の融液滴や固体粒を均一に分散

させ、且つ、埋設されたTi合金材料を適当に分散して担持する担持体として働く。この焼結防止剤はアルミナ粉がよい。

【0017】また塩化アンモニウムは、Ti合金材料表面の酸化物付着物を溶融除去する融剤として、また上述のように、AlとCrのTi系合金表面への移送体として働き、その配合量は0.5~5%とする。5%を超えて配合すると塩化アンモニウムは昇華して、損失を生じるので適当ではない。

10 【0018】Al-Cr複合拡散被覆処理の温度は、1000℃~1300℃の範囲が適当であって、処理温度1000℃より低いと、Ti合金表面からAl及びCrが十分に拡散せず、形成されるAl-Cr複合拡散被覆層が薄くなるので、十分な耐酸化性が得られない。また1300℃を超えると、Al-Cr合金固体や焼結防止剤の粉末が、Ti合金表面に付着して、肌荒れを生じ、平滑表面が得られない。

【0019】

【実施例】Al-Cr複合拡散被覆処理剤のアルミニウム粉及びクロム粉の配合量を変えて、Ti-Al合金に20 Al-Cr複合拡散被覆処理を行い、Al-Cr拡散被覆層を形成する試験を行った。

【0020】Al-Cr複合拡散被覆処理剤は、アルミニウム粉を5~40%、クロム粉を0~40%の範囲で調整し、塩化アンモニウムを0.5%の一定の配合とし、残部の焼結防止剤として、アルミナ粉末を使用して調製した。

30 【0021】供試材は、Ti合金には、耐熱用のTi-34wt%Al合金を使用し、直径8mm、長さ10mmの円柱形状の試片に加工した。

【0022】上記Al-Cr複合拡散被覆処理剤を鋼製容器に装入して、上記の試片を当該処理剤中に埋設し、900℃~1400℃の温度に加熱しアルゴン雰囲気ガス中で10時間保持して、Al-Cr複合拡散被覆処理を行った。

【0023】この処理後の試片の表面性状を観察し、その断面の顕微鏡観察により、Al-Cr拡散被覆層の厚みを測定し、さらにEPMAにより表面のAl濃度とCr濃度を測定した。

40 【0024】Al-Cr複合拡散被覆処理後の試片の被覆層表面は肌荒れ状の粗面を呈するものと綺麗な平滑面を呈するものがあった。そこで、試片の被覆層表面を走査型電子顕微鏡(SEM)により観察した。図2

(A)は、粗面を呈した試片(試料番号1)のSEM写真であるが、表面に突出分布した粗大な粒長約100μmの粒状物が観察される。同図(B)の試片(試料番号2)は、試片表面に肌荒れを生じているが、表面粒状物は微細化している例である。同図(C)は肌荒れのない表面性状の良好な試片(試料番号10)のSEM写真で、表面の粒状物は粒径2μm以下で細密化している。

SEM観察結果からこの被覆層表面の粒状物が微細化するほど試片の表面は緻密平滑化することが判った。即ち、Al-Cr複合拡散被覆処理後の表面性状は表面の粒状物の粒径に依存している。

【0025】次に、Al-Cr複合拡散被覆処理をした上記試片を大気中1000℃の温度で100時間加熱保*

*持して、耐酸化性試験を実施し、その試片の加熱前後の重量差から、酸化増量を算出して、Al-Cr拡散被覆層の耐酸化性を評価した。試験結果をまとめて表1に示した。

【0026】

【表1】

試料 番号	処理剤量		処理温度	Al-Cr 拡散被覆層				* 酸化増量 mg/cm ²
	Al粉	Cr粉		Al濃度	Cr濃度	層 厚	表 面	
1	20%	0%	1200℃	62.0%	0%	180μm	荒	4.8
2	10	40	1200	41.5	9.8	40	荒	25
3	5	20	1200	39.5	2	55	不均質	36
4	40	20	1200	63.2	0.8	140	荒	8.9
5	30	15	900	58.4	0	15	良	10.5
6	10	15	1400	57.0	1.8	160	荒	4.9
7	10	10	1100	57.8	0.5	60	良	3.0
8	10	10	1200	52.8	2.8	90	良	0.3
9	30	10	1200	60.0	0.8	140	良	1.0
10	10	30	1200	51.1	4.9	60	良	0.8
11	30	30	1100	62.2	8.9	100	良	3.3

*1000℃×100時間大気中加熱

【0027】また、表面性状と耐酸化性をAl-Cr複合拡散被覆処理剤中のアルミニウム粉量とクロム粉量の関係において図示したものが図1である。図中で、酸化増量5mg/cm²以下をもって、耐酸化性良好と判断した。

【0028】図1中に実線で囲んだ範囲が、本発明のAl-Cr複合拡散被覆処理剤の配合範囲である。1000～1300℃の温度において、表面性状と耐酸化性の両面から処理剤のこの配合範囲がよいことが判る。

【0029】次に、アルミニウム粉とクロム粉の全量に代えて、Al-Cr合金粉を使用した実施例を示す。A 40

1-Cr合金粉 (Al含有量75%、Cr含有量25%

30%)を40%、塩化アンモニウム0.5%、残部アルミナ粉を配合して、Al-Cr複合拡散被覆処理剤とした。Al-Cr合金粉のこの配合は、アルミニウム粉30%、クロム粉10%の配合に相当する。

【0030】この処理剤に、直径8mm、長さ10mmのTi-34wt%Al合金の試片を埋設して、1200℃×10時間のAl-Cr複合拡散被覆処理を行い、その後、1000℃×100時間の耐酸化性試験を行った。結果を表2に示すが、Al-Cr複合拡散被覆層の表面性状及び耐酸化性いずれも良好である。

【0031】

【表2】

試料 番号	AlCr合金粉		処理 温度	Al-Cr 拡散被覆層				* 酸化増量 mg/cm ²
	Al量	Cr量		Al濃度	Cr濃度	層 厚	表 面	
21	30%	10%	1200℃	60.4%	1.0%	150μm	良	1.0

*1000℃×100時間大気中加熱

【0032】

★r複合拡散被覆処理剤により、Ti系合金のAl-Cr

【発明の効果】本発明のクロム粉末を配合したAl-C★50 複合拡散被覆処理を実施すれば、Ti系合金のCrを含

有するAl-Cr拡散被覆層により、耐酸化性が改善され、Ti-14~36%Al合金においては、その最高使用温度を1050℃まで高めることができる。

【0033】同時にAl-Cr拡散被覆層表面は平滑なきれいな表面とすることが容易にできるから、例えばタービンプレードとして使用する場合には何ら表面研磨をしなくても、タービンの回転効率を低下させることなく使用でき、また表面の精密研磨を実施する場合でも、削り代を薄くすることができ、必要以上にAl-Cr拡散被覆層を厚くする必要がないから拡散被覆処理工程を

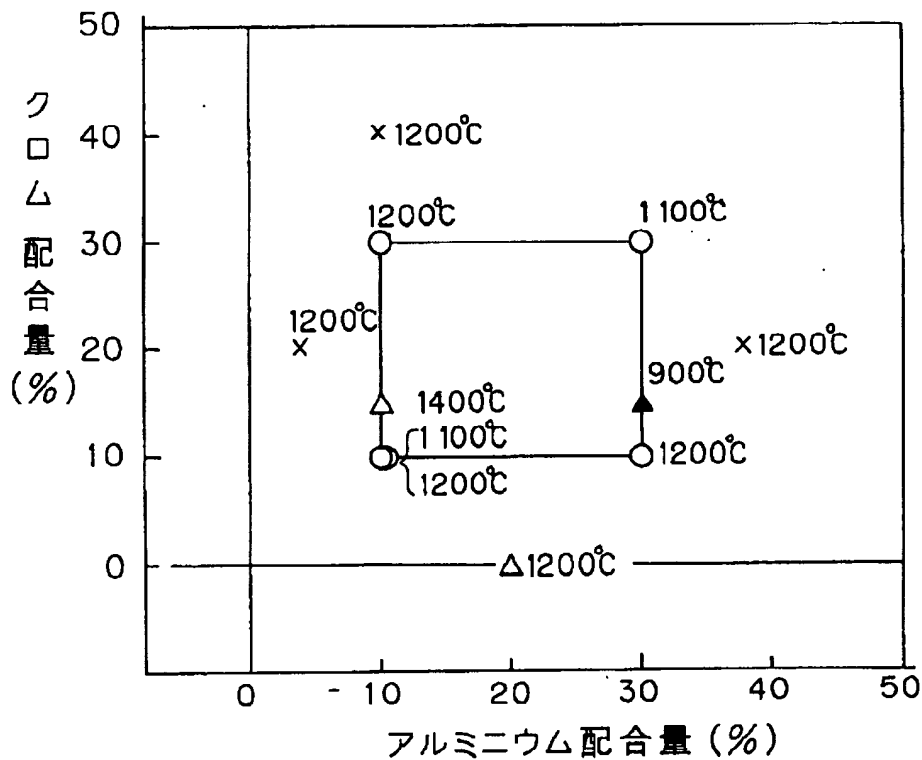
簡素化し、精密研磨工程を簡素化または省略することができる。

【図面の簡単な説明】

【図1】Al-Cr複合拡散被覆処理剤中のアルミニウム粉量とクロム粉量及び拡散被覆処理後の表面性状と、耐酸化性試験の酸化増量の関係を示す図。

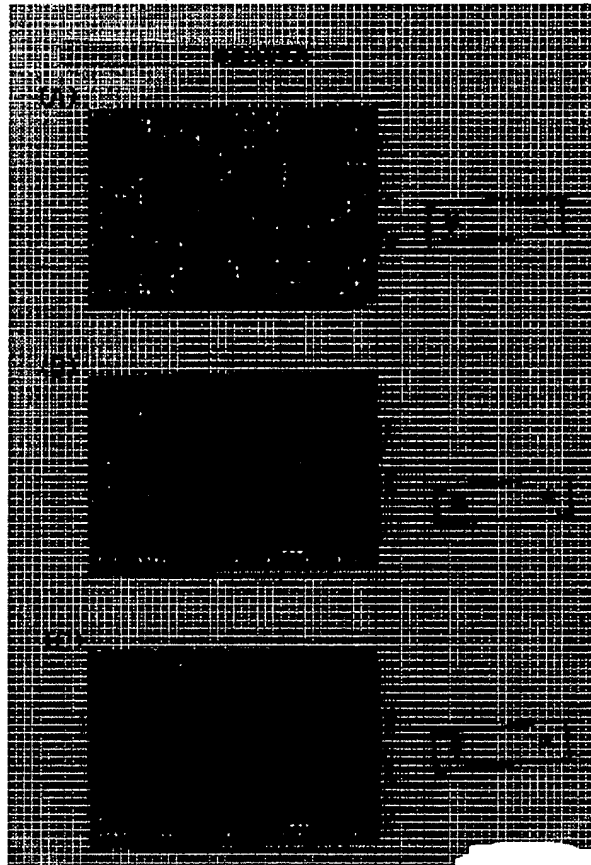
【図2】(A)、(B)及び(C)は、それぞれ、試料番号1、2及び10についてのAl-Cr複合拡散被覆処理後の試験片の拡散被覆層表面の走査型電子顕微鏡による金属組織写真(いずれも倍率;70)。

【図1】



	表面性状	耐酸化性
○	良好	良好
△	不良	良好
▲	良好	不良
×	不良	不良

【図2】



フロントページの続き

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